# PREPARATION, CHARACTERISATION AND APPLICATION OF ACYLATED-CHITOSAN MATRIX

**A PROJECT REPORT**

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## BONAFIDE CERTIFICATE

Certified that this project report **"PREPARATION, CHARACTERISATION AND APPLICATION OF ACYLATED-CHITOSAN MATRIX"** is the bonafide work of "**DISHA GUPTA (1110204009) and REVATHY R (1110204038)"** who carried out the project work under my supervision.

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# ABSTRACT

The removal of reactive red dye solution using butyl-chitosan matrix was studied in this project. Commercially available chitosan was chemically modified using butyraldehyde to prepare butyl-chitosan. The prepared butyl-chitosan was characterised using Fourier Transform Infrared Spectroscopy (FTIR). The dye removal studies were carried out by both batch and continuous mode. Contact time, pH, temperature, initial dye concentration and adsorbent dosage were varied for the batch adsorption study. It was found that the optimum conditions for the adsorption of reactive red on butyl-chitosan were pH 7, 0.1 g of butyl-chitosan/ml, 30 ppm dye concentration, 30°C for 20 min without agitation and the maximum dye removal was 67.5%. Studies were also carried out in continuous mode using column packed with butyl-chitosan. The dye solution was given as the mobile phase. It was found that the maximum dye removal for the fraction between 7 min and 30 min time interval was 96.77%. At the end of 2 h, the percentage dye removal was 90.32. This showed the possibility of scaling-up of butyl-chitosan for dye removal at industrial level.

*Keywords:* Butyl-chitosan, reactive red, hydrophobic interaction column, adsorption, dye removal

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| | |
|---|---|
| min | Minutes |
| h | hour |
| g | gram |
| ppm | Parts per million |
| HIC | Hydrophobic interaction chromatography |
| Q | Adsorption capacity |
| DR | Dye removal |
| IR | infrared |
| XRD | X-Ray diffraction |
| SEM | Scanning electron microscope |
| TGA | Thermogravimetric analysis |
| NMR | Nuclear magnetic resonance |
| FTIR | Fourier transform infrared spectroscopy |
| SDS | Sodium dodecyl sulphate |

# CHAPTER 1
# INTRODUCTION

## 1.1    MOTIVATION

Textile dyeing effluent is one of the major pollutants from textile industry in India. The dyes are highly recalcitrant in nature, resistant to aerobic digestion and stable to oxidizing agents. This poses great threat to human health and wildlife. Dyes affect photosynthetic activity significantly in aquatic life since it reduces light penetration. The colour and the breakdown products of dye containing effluents are highly toxic, carcinogenic or mutagenic to life forms because of the presence of carcinogens such as benzidine, naphthalene and other organic compounds. This is why the discharge of dyeing effluents into the water environment is undesirable (Rajeswari *et al*., 2013).Thus recycling of treated waste water due to high levels of pollutants has been recommended in dyeing and finishing processes.

## 1.2    GENERAL

Dyes are colouring materials that differ in chemical composition and are used for imparting colours to materials such as paper, fabrics, leather, etc. Dyes impart colour due to their affinity for the substance. Dyes are generally applied in aqueous solutions and at times using organic solvents. Textile industry is one of the major sectors employing dyes for their products. The other industries where dyes are used in a variety of products include pulp and paper, art supplies, adhesives, beverages, ceramics, construction, food, cosmetics, glass, paints, polymers, soap and more.

There are over 100,000 varieties of dyes available in the market (Daneshvar *et al*., 2007). Industrially, dyes are classified as acidic, basic, azoic, vat, direct, disperse, mordant, reactive, solvent and sulphur dyes. The commonly used dyes in textile industry are the azo dyes. Azo compound class accounts for 60-70% of all dyes. Azo dyes are characterised by the presence of azo group (-N=N-). Azo dyes are available in a wide range of colours. Azo dyes are cost effective and have good fastness properties.

## 1.2.1 Current Scenario

The annual production of dyes in the world is almost one million ton; of which azo dyes represent about 70% (by weight).The production of dye stuffs and pigments in India is nearly 80,000 tons. India is the second largest exporter of dyestuffs next to China. The textile industry accounts for largest consumption of produced dyes which is nearly 80% (Saranraj 2013). The textile industry generates highest amount of wastewater. With more than 3600 individual textile dyes being manufactured and around 8000 chemicals being used, the textile industry stands as one of the major polluters of clean water. The water consumption of an average sized textile mill producing 8000 kg fabric per day is 1.6 million litres per day (Kant 2012).

With increasing demand for textile products, there is a proportional increase in the waste water generation, thus increasing the waste water discharge. Hence there is an overall increase in pollution in the receiving water bodies. It is estimated that 1.5 million litres of dye effluent is discharged by an average mill in India per day (Srinivasan *et al*., 2014). In Tirupur, there are about 3000 hosiery units consuming 1, 00,000 $m^3$ water per day. Approximately, 75,000 $m^3$ of effluents are

discharged each day from these units (Rajeswari *et al*., 2013). This discharge contains several toxic chemicals such as dyes, acids, alkalis, dispersants, etc. The organic stuffs and chrome dyes in these effluents contain chemicals such as chromium, zinc, copper, sodium and potassium which pose as the major pollutants in waste waters. These raise a serious problem for the aquatic animals and also for human consumption.

### 1.2.2    Different methods for dye removal

Dyes are highly recalcitrant in nature and thus are difficult to be degraded by conventional treatment methods. Various physical, chemical and biological methods are designed for removal of dyes from dye effluents before being discharged into the water bodies. Each method has its own advantages and disadvantages. Few methods available are;

Membrane filtration processes (reverse osmosis, nano-filtration, ultrafiltration, microfiltration, and electrodialysis) and various adsorption techniques are the physical processes for dye removal. These processes are rapid and effective in removing all types of dyes and producing high quality treated effluent. The major disadvantages associated with membrane processes are pre-treatment of effluent to reduce salt load, limited membrane lifetime, and membrane fouling and expensive. These membrane based separations cannot be used with high amount of slurries as well. It is also reported that adsorption is the effective and best process for dye removal for waste water (Kharub 2012).

The commonly used chemical processes for dye removal are oxidative process, ozonization, electrokinetic coagulation, coagulation and flocculation combined with floatation and filtration, irradiation and electrochemical processes. These chemical processes are effective in dye removal but are also expensive. Also these processes cannot be carried out for large amounts of effluents. Another disadvantage with these methods is the disposal problem due to formation of high amounts of concentrated sludge (secondary pollutant). Due to high demand for electrical energy and chemicals, these methods are not preferred for dye removal (Kharub 2012).

The biological methods used for dye removal are decolourisation by white-rot fungi, adsorption by living/dead microbial biomass and likewise (Kharub 2012). These methods are cost effective and have flexible design. But at the same time, these methods are slow and do not show satisfactory colour removal. These methods also have disadvantage with requirements of specific conditions and high sludge production. Live cells and enzymes cannot be used due to high pH and salts in textile dyeing effluents.

## 1.3     ADSORPTION

Adsorption is surface phenomena that occurs when a gas or a liquid accumulates on the surface of a liquid or a solid which is the adsorbent, forming a molecular film which is the adsorbate. Adsorption is different from absorption. Absorption is a process in which a substance diffuses into a solid or a liquid to form a solution. Desorption is the reverse process. Adsorption is a bulk phenomenon where all the bonding requirements of the atoms are filled by the atoms in the material. Generally adsorption is classified as physisorption and chemisorption.

Physisorption is the characteristic of weak van der Waal's forces which is responsible for the non ideal behaviour of real gases. Physisorption has low heat of adsorption. In physisorption, the adsorption takes place in monolayer or multilayer. The characteristics of physisorption are that they are non specific, not activated, reversible and have low activation energy and also low heat of adsorption (Benavente 2008).

Chemisorption is the characteristic of chemical bonding. Unlike physisorption, in chemisorption, the adsorption takes place only in monolayer. They have high activation energy and high heat of adsorption. The adsorbate interacts with the surface strongly with the help of a covalent bond. Chemisorption is reversible only at high temperatures (Benavente 2008).

Adsorption is usually described through isotherms which give the amount of adsorbate on the adsorbent as a function of its pressure or concentration at constant temperature. Among the 15 isotherm models, Langmuir and Freundlich isotherm model are quite often used.

## 1.4 HYDROPHOBIC INTERACTION CHROMATOGRAPHY

Hydrophobic Interaction Chromatography is a separation technique that uses the properties of hydrophobicity to separate proteins from one another. In this type of chromatography, the hydrophobic groups such as phenyl, octyl, or butyl, are attached to the stationary column. It is sensitive enough to be influenced by non-polar groups which are buried within the tertiary structure of proteins but exposed if the polypeptide chain is incorrectly folded or damaged. This sensitivity makes them useful for separating the pure native protein from other forms.

The HIC column consists of non-polar stationary and polar mobile phase. The analyte is distributed between the mobile and stationary phases. HIC involves hydrogen donor interactions between the neutral polar species as well as weak electrostatic mechanisms under the high organic solvent condition which is used for retention. The more polar compounds have greater affinity towards the stationary phase and will interact within it than the less polar compounds. Thus, in HIC the separation occurs based on the polarity of the compounds and the solvation. Since textile effluent is rich in salts, binding of dye in the effluent is favourable with hydrophobic portion of the ligand with the stationary phase.

## 1.5    HIC MATRICES FROM SEPHAROSE

The trade name for cross linked, bead-form of agarose is sepharose. Sepharose is a polysaccharide material obtained from seaweed. The most common application for sepharose is in chromatographic separations of bio molecules. Sepharose is also used to immobilize enzymes, proteins, peptides and also antibodies. Butyl-sepharose, octyl-sepharose and phenyl-sepharose are some of the types of HIC matrices. These matrices were successfully used to separate a variety of dyes from both simulated and real textile dyeing effluents (Ramalingam *et al*., 2013).

Butyl-sepharose is used during the initial stages of a separation process to remove the bulk of impurities without stringent requirements for conditioning of the sample. Butyl-sepharose is used as hydrophobic interaction chromatography (HIC) matrix. Butyl-sepharose is rigid, highly cross-linked, and forms porous agarose beads which

permit high flow rates at moderate pressure and also has a high loading capacity. Octyl-sepharose is a highly cross-linked agarose bead that gives an excellent flow property to the medium in the hydrophobic interaction chromatography. Phenyl-sepharose is also used as hydrophobic interaction chromatography matrix to separate membrane-bound proteins. They are mostly used during the intermediate stages of separation processes when high flow rate is required.

## 1.6     CHITIN AND CHITOSAN

Chitin (poly($\beta$-(1-4)-N-acetyl-D-glucosamine) is a natural nitrogenous polysaccharide which is synthesised by enormous number of living animals. It is the second most abundant polymer next to cellulose. Chitin forms the structural components in the exoskeleton of arthropods and also as cell wall components of fungi and yeast. They are present as ordered crystalline micro fibrils. It is a white, hard, inelastic and inert solid. It is highly hydrophobic and insoluble in water and organic solvents. Depending on the source, there are three polymeric forms of chitin: $\alpha$-chitin (crab and shrimp shells), $\beta$-chitin (squid pen) and $\gamma$-chitin (stomach cuticles of cephalopods) (Jang *et al*., 2004). Despite the widespread occurrence, chitin for commercial purposes is extracted from crab and shrimp shells (Rinaudo 2006). The process of extraction of chitin from the shells is explained by (Burrows *et al*., 2007). Chitin may be described as cellulose with one hydroxyl group on each monomer replaced by an acetyl amine group. This facilitates enhanced hydrogen bonding and greater matrix strength. When the degree of deacetylation of chitin drops below 50%, it becomes soluble in acidic media and is called chitosan (Rinaudo 2006).

Chitosan is a linear nitrogenous polysaccharide composed of randomly distributed units of β-(1-4- )-linked D-glucosamine and N-acetyl-D-glucosamine. It is also naturally present in fungi and yeast (Sailaja *et al*., 2010). Industrially, chitosan is produced by deacetylation of chitin using sodium hydroxide. Chitosan can also be produced by enzymatic deacetylation using lysozyme, chitin deacetylase, neutral protease and snailase. Chitin is found insoluble in most solvents whereas chitosan is soluble in most organic acidic solutions with pH below 6.5. Chitosan is well known for its biodegradability, biocompatibility and non-toxic nature (Mi *et al*., 2002) and thus it used in various drug delivery studies (Rani *et al*., 2010). It also shows antimicrobial properties and also inhibits the growth of a wide variety of fungi, bacteria and yeast. This property is being employed in biomedicine studies (Goy *et al*., 2009). It can also bind toxic metal ions and thus can be used for air cleaning and water purification applications (Neto *et al*., 2013).
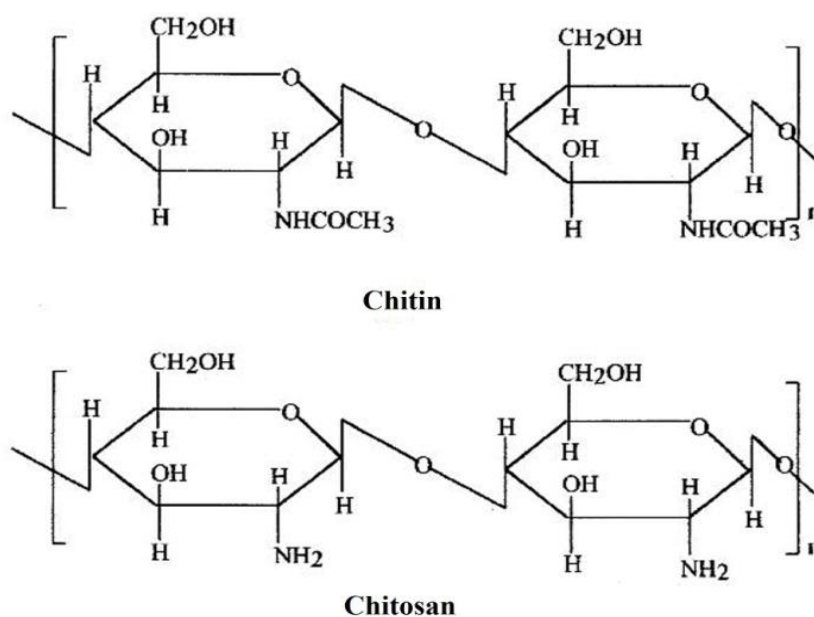
**Figure 1.1 Structure of chitin and chitosan**

## 1.7    OBJECTIVES

The main objectives of this work are:

- To prepare acylated chitosan as hydrophobic interaction chromatography (HIC) matrix.

- To characterise the modified chitosan matrix, and

- To test the ability of the chitosan- HIC matrix for the selective removal of dyes from textile dyeing wastewater.

# CHAPTER 2
# REVIEW OF LITERATURE

## 2.1      GENERAL

Kofuji *et al*., (2000) performed controlled release of prednisolone, as a model drug, using biodegradable chitosan gel beads. Drug release profile and enzymatic degradation of chitosan gel beads were investigated. Chitosan properties like degree of deacetylation were found to affect degradability of chitosan gel beads. The chitosan gel beads loaded with prednisolone sustained significantly when compared to chitosan beads prepared with sodium hydroxide only. But the sustainability was not maintained with increasing sodium hydroxide concentration used for preparing the beads. Controlled drug release from chitosan beads was also investigated by using a complex formed between chondroitin sulphate and chitosan. After coupling with chondroitin sulphate, the release was prolonged with no change in the treatment time. It took 5min for 50% drug release with prednisolone powder and about 200min with chitosan gel beads with 10% glycine (pH 9.0) and 330min with chondroitin sulphate coupled beads with 10% glycine (pH 9.0). It was concluded that chitosan gel beads can be used as promising vehicles for sustained drug delivery.

Kannan and Sundaram (2001) conducted a comparative kinetics and mechanism study on the removal of methylene blue on various carbons by adsorption. The adsorbents used were commercially available activated carbon and prepared activated carbons from bamboo

dust, rice husk, and straw and groundnut shell. In order to obtain information on the treating dye effluents, various experimental parameters were checked. It was found that with increase in pH, contact time and amount of adsorbent, there was an increase in extent of dye removal and also with decrease in particle size and initial dye concentration; there was a significant increase in dye removal. The adsorption process with these carbons fitted the Langmuir and freundlich isotherms and kinetics studies revealed that the process followed first order kinetics. The comparison of indigenous activated carbon with the commercial activated carbon revealed that the indigenous activated carbon can be used as low cost alternative sources for dye removal from wastewater and dyeing effluents.

Yaseen *et al*., (2006) carried out a project to design a new extended release gastro retentive mutiparticulate delivery system for verapamil by incorporating into hydrogel beads that is made of chitosan. They formed beads by dropping solutions of verapamil and chitosan in a solution of tripolyphosphate with the help of a syringe pump with adjustable constant rate. They cross linked the formed beads with glutaraldehyde and the excess glutaraldehyde was washed. The physical properties and the floating characteristics of the prepared beads were studied. The drug loading efficiency was found to be around 42%. They exhibited a kinetic model of combined mechanism of diffusion partially through a swollen matrix and partially through water-filled pores. Thus they concluded that the beads can be used for controlling the release of drugs.

Filipkowska (2006) conducted an experiment to test the efficiency of reactive dye adsorption onto chitin and chitosan beads.

They aimed to determine a beneficial method for preparing chitin in respect of its adsorption capacity which would provide a high removal efficiency of dyes. They analyzed the efficiency of black B and black DN adsorption from aqueous solutions onto chitin and chitosan. The analyzed the results with Langmuir model. They observed that chitosan in the form of beads showed a better adsorption capacity and was characterized by slightly lower adsorption affinity and it demonstrated considerably better mechanical and sedimentation properties. And also they found that chitin with a low deacetylation degree; both dyes tested were demonstrated to display a high affinity to the adsorbent. They concluded that with an increasing degree of deacetylation, the affinity of dye to chitin increased.

Gomez *et al*., (2007) performed kinetic and adsorption studies for acid dyes using activated carbon. The dyes chosen for the study were Acid Orange 61, Acid Red 97 and Acid Brown 425. The adsorption studies were carried out at room temperature (25°C). In order to obtain information on adsorption characteristics of the different dyes, the experiments were carried with respect to contact time. The experimental data revealed that the desorption kinetics with activated carbon follows pseudo second order kinetics model. Except for Acid Orange 61, the other dyes had their experimental isotherms of S-type in terms of Giles classification. The best fit for the isotherms was for freundlich model. It was also evident that in the mixture of dyes, the adsorption was highest for Acid Red 97. A comparative study was also carried out with simple and mixed dyes and was concluded that some of the dyes can affect the behaviour of other in the adsorption process.

Burrows *et al*., (2007) addressed the environmental concern of improper disposal of seafood wastes and performed studies on extraction of chitin and chitosan from crab exoskeleton and evaluation of chitosan as a seed fungicide and plant growth enhancer. Chitin was obtained by shell meat removal followed by demineralization using hydrochloric acid or acetic acid. From this chitosan was prepared by deacetylation using sodium hydroxide. Black-eyed peas exposed to different chitosan concentrations were used for growth enhancement study. Anti-fungal experiment was carried out with peanut seeds infested with *Penicillium.* The required data were generated using PROC ANOVA and PROC general linear model statistical systems. The data generated indicated that seeds pre-treated with chitosan extracted with 0.5% hydrochloric acid had best overall growth and was also efficient in eliminating fungus from sea foods. It was concluded that there are plausible possibilities of utilising seafood waste for agricultural purposes.

Gupta and Suhas (2009) reviewed the application of several low-cost adsorbents for the purpose of dye removal. The increasing demand for low cost and efficient treatment methods has lead to investigation of various natural materials as low cost adsorbents. In this review, several natural, industrial and synthetic materials are studied as low cost adsorbents for application in dye removal. Also, other methods used for dye removal from water and wastewater were investigated. It was also reviewed that low cost adsorbents in addition to having wide availability, have appreciable adsorption capabilities and fast kinetics too. From the literature review it is clear that in the past few decades there has been increase and production and utilization of dyes, thus being a big threat of pollution. It was concluded that though many

techniques are available for dye removal, there is no such technique that can successfully remove all dye at low cost. It was observed that adsorption is very efficient when compared to other processes for dye removal. Due to high cost of activated carbon, the interest for adsorbents has shifted towards low cost natural adsorbents.

Rangel-Vazquez *et al*., (2010) synthesised and characterised chitosan coated dialdehyde cellulose showing antimicrobial properties. Chitosan coated dialdehyde cellulose was prepared by oxidation of cotton fabric with 0.1M sodium periodate at 25°C under dark conditions for 24h with subsequent chitosan treatment for 2h at 75°C. Fourier Transform Infrared Spectroscopy (FTIR), moisture content analysis, Thermo Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) were used for characterisation of the resulting material. Presence of chitosan was confirmed using FTIR and moisture content analysis. The chitosan coated dialdehyde cellulose showed antimicrobial power of about 50% which confirmed its usage for medical applications.

Copello *et al*., (2011) performed the removal of dyes from water by sol-gel method using chitosan hydrogel/$SiO_2$ and chitin hydrogel/$SiO_2$ hybrid materials. In this paper, the adsorption capabilities of chitin and chitosan for removal of four different dyes namely Remazol Black B, Erythrosine B, Neutral Red and Gentian Violet. This was done in order to evaluate the better efficiency of chitin as a biosorbent than chitosan due to its low cost and higher efficiency. The characterisation of hybrid materials was done using Attenuated Total Reflectance- Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Scanning Electron Microscopy (SEM). The adsorption was pH

dependant. The studies were carried out using Langmuir, Freundlich and Dubinin-Radushkevich model. It was concluded that the chitin containing matrix had similar or higher adsorption capacity when compared with chitosan matrices.

Shen *et al*., (2011) used magnetic chitosan-Fe (III) hydrogel to propose a fast and highly efficient method for the removal of dyes under alkaline conditions. They prepared Chitosan-Fe (III) hydrogel by a chelation procedure with cheap and environmentally friendly chitosan and iron salts. The adsorption of dye to chitosan-Fe (III) hydrogel was found to be fast in a wide pH range, and it was also found that it agreed well to the Langmuir and Freundlich adsorption model with a high maximum adsorption capacity. The desorption studies were also performed. The dye was efficiently desorbed using NaOH which showed the high efficiency of desorption and regeneration. They concluded that the magnetic chitosan-Fe (III) has high adsorption efficiency and can be used for alkaline dyeing effluent.

Jayakumar *et al*., (2011) performed studies on drug delivery and tissue engineering applications of chitosan and its derivatives. The poor solubility of chitosan in water and in organic solvents limits its utilization for specific application. In order to improve its properties, chemical modification of the chain by coupling certain functional groups were performed. It was concluded that chitosan can be used effectively for gene delivery due to its cationic properties. Also, hydrophobic group conjugated chitosan could self assemble and encapsulate poorly soluble drugs unlike unconjugated chitosan. Chitosan forms weak 3D scaffolds for tissue engineering applications but when substances like collagen are included in chitosan, the

mechanical strength of scaffold increases. Therefore the chemically modified chitosan showed better efficiency in drug delivery and tissue engineering applications when compared to chitosan.

Bobu *et al*., (2011) synthesised and characterised N-alkyl chitosan for papermaking application. Chitosan is used for papermaking due to its properties such as Cationic polyelectrolyte behaviour and high affinity for the cellulose fibre surface. They aimed at obtaining and characterizing a water-soluble chitosan derivative by introducing alkyl groups along the chitosan chain, to confer to it hydrophobic nature, without affecting significantly its cationic character. They obtained the N-alkyl chitosan derivative by using reductive amination, also investigated it by spectroscopic techniques such as FTIR, HNMR, NMR and MS ionic charge and density solubility in water. They found that the alkylated chitosan was completely soluble in water under room temperature and neutral pH.

Huang *et al*., (2011) performed chemical modification of chitosan with tetraethylenepentamine. This chemically modified chitosan was utilised for study of anionic dye removal (eosin Y) exploiting the contribution of amino groups in adsorption. The study was carried out as a function of initial pH, agitation period, and initial concentration of eosin Y, particle size, agitation rate, adsorbent dosage and temperature. In order to fit the adsorption data, Langmuir and Freundlich isotherms were utilised. From the experimental data, it was evident that it follows Langmuir isotherm giving a maximum adsorption capacity of 292.4 mg/g at 298 K. Kinetic studies with the adsorption data showed that it followed pseudo second order kinetic model. From the thermodynamic studies showing a negative enthalpy ($\Delta H°$) and free

energy change ($\Delta G°$) value, it was clear that the adsorption process was spontaneous and endothermic in nature.

Monier *et al*., (2012) studied the use of cross-linked magnetic chitosan-2-aminopyridine glyoxal Schiff's base resin for adsorption of Cu (II), Cd (II) and Ni (II) ions. The removal of these ions is pH dependant and optimum adsorption occurred at pH 5.0. The estimated initial rate of adsorption was 2.7, 2.4 and 1.4mg/(g min) for Cu (II), Cd (II) and Ni (II) ions respectively, thus showing a fast adsorption rate in all the three cases. Langmuir, Freundlich and Tremkin isotherms were used for interpretation of adsorption data. The maximum adsorption capacities observed with Langmuir isotherm model were $124 \pm 1$, $84\pm2$ and $67 \pm 2$ mg $g^{-1}$ for Cu (II), Cd (II) and Ni (II) ions respectively. Also from the studies performed it was known that the adsorption process in this case could be defined by pseudo second order kinetic model. Thermodynamic studies showed spontaneity, feasibility and exothermic nature of adsorption. The regeneration of adsorbent was done using hydrochloric acid and EDTA solutions.

Yamani *et al*., (2012) developed chitosan beads impregnated with mixed metal oxide containing crystalline $Al_2O_3$ and nanocrystalline $TiO_2$. This adsorbent was found to have high capacity removal of arsenite than mixed oxide alone. Maximum arsenite removal was obtained by optimizing the composition of beads using UV light. The mechanism of removal was investigated and a mode of action was proposed wherein $TiO_2$ oxidizes arsenite to arsenate which is then removed from solution by $Al_2O_3$. This mechanism was validated by pseudo –second order kinetics. It was found that mixed metal oxide

chitosan beads showed more removal capacity of arsenite than $TiO_2$ chitosan beads.

Zhang *et al*., (2012)synthesised a chitosan derived by the dispersible nano $SiO_2$ and succinic anhydride. This derivative was characterised by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The thermal activity was determined but thermo gravimetric studies. They also studied the effects of various parameters such as adsorbent dosage, ph, initial dye concentration and temperature. The adsorption equilibrium fitted Langmuir isotherm and the maximum adsorption capacity for monolayer saturation was found. Thus, they concluded that the chitosan derivative showed more adsorption capacity than the chitosan at optimum conditions.

Fan *et al*., (2013) performed dye adsorption and removal using magnetic β-cyclodextrin-chitosan/graphene oxide synthesized as nanoadsorbent. It was observed that due to hydroxyl and amino functional groups on chitosan and magnetic property of $Fe_3O_4$, the adsorbent possess versatile and good adsorption capacities for dye. It was also shown that it can easily be extracted from water by magnetic attraction. Another observation was that the adsorbent can be easily regenerated for reuse with hardly any changes in the adsorption capacity. Langmuir isotherm model best fitted the adsorption characteristics study data of the adsorbent. Also the kinetics study carried out indicated that the data follows pseudo second order kinetics model. The thermodynamics study data revealed that the process is spontaneous and endothermic in nature. Since the adsorbent was nano structured, it showed advantageous properties like good adsorption

capacity, rapid extraction, easy and handy operation and regeneration. This proved to be an efficient adsorbent for dye removal from wastewater.

Lv *et al*., (2013) carried out the preparation of dialdehyde chitosan and used it for Green synthesis of silver nanoparticles. The dialdehyde chitosan was used as a stabilizing and reducing agent. Chitosan was oxidised using sodium periodate to form dialdehyde chitosan and it was characterized using elemental analysis and H-NMR. Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and UV-vis spectroscopy was used for characterisation of silver nanoparticles. FTIR spectra showed that the major agents that stabilized silver nano particles were the aldehyde and amino groups. Silver nano particles of 30-40nm in size were dispersed in solution. It was hypothesised that formation of four coordinate complexes could have lead to the stabilization of silver nano particles. The synthesised silver nano particles had stability period of more than three months.

Neto *et al*., (2013) studied the preparation and evaluation of Iron (III) immobilized chitosan beads for removal of As (III) and As (V) from water. The adsorption studies of As (III) and As (V) on chitosan were carried out in batch and in columns at pH 7.0. The maximum adsorption capacities by Langmuir adsorption model for As (III) and As (V) were 21.24 and 27.59 mg g$^{-1}$, respectively. Good results were obtained with column studies because of its use at neutral Ph. Based on the results it was concluded that iron (III) immobilized chitosan beads were effective in As (III) and As (V) removal from groundwater, river water and mine water.

Chatterjee *et al*., (2013) used chitosan hydrogel beads for the adsorption of a cationic dye, methylene blue, generated by anionic surfactant gelation. These chitosan hydrogel beads were formed using sodium dodecyl sulphate (SDS) gelation and were used for the removal of the cationic dye, methylene blue. When prepared by alkali solution the chitosan beads showed low adsorption capacity due to the charge repulsion between the beads and methylene blue. The adsorption capacity chitosan hydrogel beads decreased when the SDS concentration was increased which lead to increase in their density. They found that the increase in initial pH of chitosan beads and chitosan hydrogel beads lead to increased adsorption of methylene blue. They concluded that the adsorption of a cationic dye, methylene blue , by chitosan hydrogel beads which was formed by anionic surfactant gelation, was more than that for chitosan hydrogel beads formed by conventional alkali gelation. This difference was due to a reduction in charge repulsion between chitosan and methylene blue and an increase in hydrophobic interactions between methylene blue and SDS.

Batista *et al*., (2013) produced eco-friendly chitosan by *Syncephalastrum racemosum* and applied it for the removal of Acid Orange 7 from wastewater. In this paper, agro-chemical residues were used for the production of microbiological chitosan and this chitosan was used for removal of acid orange 7 from wastewaters. From the results it was evident that corn steep liquor, an agro-industrial residue can be used for the production of microbiological chitosan that yields up to 7.8 g/kg of substrate. Fourier Transform Infrared Spectroscopy (FTIR) was employed for the confirmation of peaks for chitosan. The efficiency of removing acid orange 7 of prepared microbiological chitosan in distilled water was 89.96% and that in tap water was

80.60%. This was significantly higher than the results obtained from conventional chitosan prepared from crustacean exoskeleton. Thus this biopolymer is advantageous in terms of cost and efficiency for removal of dyes from wastewater. But this biopolymer is applied only for low concentrations of dyes which are also considered toxic as a water pollutant. Another advantage of this microbiological chitosan is that high percentage recovery of acid orange 7 is possible with it, thus it can be reusable.

Saifuddin *et al*., (2014) performed purification of glycerol from biodiesel production using yeast immobilised chitosan through adsorption and microwave assisted acidification. This method was found effective than the conventional methods. The advantage of this treatment is recovery of high amounts of glycerol and low operation cost. The purification starts with microwave assisted acidification process and then utilises biosorbent prepared from dead yeast cells immobilized on chitosan. A complete colour reduction was obtained by this process. The final glycerol yield from this combined process of microwave assisted acidification and adsorption was 93.1 − 94.2%.

Yagub *et al*., (2014) presented a review article that included information of dyes, dye adsorption, characteristics of adsorbents, toxicity, classification and various treatments for removal of adsorbents. Adsorption using alternate adsorbent for dye waste treatment found to benefit water treatment and also waste management. Activated carbon from biomass was found to be an effective low cost replacement for non-renewable coal based granular activated carbon. They also presented the adsorption capacity of various adsorbents under different parameter. They also included the factors that affect the adsorption

process such as temperature, pH, adsorbent dosage and initial dye concentration. They also studied about the adsorption kinetic models and isotherm models for wide range of adsorbents.

Jabbar et al., (2014) investigated the adsorption of Congo Red from aqueous solution onto chitosan in a batch system. They studied the effects of solution pH, initial dye concentration, pH and temperature. The results showed that chitosan can be used as a biosorbent which can be used to remove the azo dyes from contaminated water. Synthesize of chitosan involved three main stages as demineralization, preconditioning, deacetylation and deproteinization. And the synthesized chitosan was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and solubility in 1% acetic acid.

Sanlier *et al*., (2014) conducted a study to prepare magnetic micro sized adsorbents which has high adsorption capacity for the removal of direct red 23. They removed the textile direct dye 23 by preparing glutaraldehyde cross linked chitosan beads. They used barium ferrite to give magnetic property to the beads so that they could be easily separated from the water after treatment. The effects of various parameters such as dye concentration, incubation time, barium ferrite, glutaraldehyde amount and pH were studied. They applied Freundlich and Langmuir models to describe the isotherm models. They compared the magnetic chitosan beads with activated carbon and found that the beads showed better results.

Maity and Ray (2014) utilised semi and full interpenetrating polymer network of polymethacrylic acid and chitosan for enhanced adsorption of methyl violet and Congo red. In this study, semi and full

IPN type hydrogels were prepared in the presence of chitosan by free radical insitu polymerization of methacrylic acid using glutaraldehyde and N,N'-methylene-bis-acrylamide as crosslinkers. These hydrogels were then characterized and utilised for removal of methyl violet and Congo red from water. It was observed that the adsorption of dyes was highest at high concentration ranges of dyes. Also, the % dye removal was higher for Congo red when compared to methyl violet. The adsorption kinetics was seen to follow pseudo second order kinetics model at low concentration range and several isotherms like langmuir, freundlich, Sip and FS model.

Wang *et al*., (2014) performed adsorption studies using different organic acid modified natural adsorbent for removal of malachite green. In this paper, *Cinnamomum camphora* sawdust modified with organic acids such as oxalic acid, citric acid and tartaric acid is used as the adsorbent. It was noted that the extent of malachite green adsorption onto the adsorbent increases with increasing pH, contact time, organic acid concentration and temperature but decreased with increasing ionic strength and adsorbent dosage. Kinetics study revealed that pseudo second order kinetics model is best suited for this adsorption process. Langmuir model best fits the equilibrium data with the maximum adsorption capacity of the three acids as 280.3, 222.8 and 157.5 mg/g respectively. The thermodynamics study data showed that the adsorption process was endothermic. It was pointed that the dye loaded adsorbents are potential sources of secondary pollutants. Hence biochar is derived from the dye loaded adsorbents to minimise the secondary pollution.

Farzana and Meenakshi (2014) produced chitosan beads impregnated with titanium oxide for the photo-decolourization and detoxification of toxic dyes. In this study, three different dyes namely methylene blue, reactive red 2 and rhodamine B are removed using titanium oxide impregnated chitosan beads by photocatalytic method. The produced titanium oxide impregnated chitosan beads were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Titanium oxide impregnated chitosan beads showed much higher photo catalytic activity when compared to titanium dioxide. Here, chitosan removes the dye molecules by adsorption and supplies the dye molecule to titanium dioxide for degradation. The experiment was carried out with different parameters such as pH, dosage, irradiation time, co-ions and substrate concentration. The kinetics studies revealed that it followed Langmuir isotherm model.

Esquerdo *et al.*, (2014) utilised chitosan scaffold, for the removal of hazardous food dyes from aqueous solutions, as an adsorbent. Since chitosan is a good alternative for the removal of dyes from wastewater but has a low surface area and porosity, chitosan scaffold was prepared for the purpose. The prepared chitosan scaffold was characterised using scanning electron microscopy (SEM), structural characteristics and infrared spectroscopy. It was shown that the chitosan scaffold presented a porosity of 92.2±1.2%, pore size from 50 to 200μm and specific surface area of $1135 \pm 2$ $m^2g^{-1}$. Equilibrium, thermodynamics and kinetic studies were carried out for the adsorption process and desorption studies were also carried out. The adsorption process followed Langmuir isotherm. Also, the adsorption process was spontaneous, favourable, and exothermic and enthalpy controlled

process. The desorption of dyes from the scaffold can be carried out with 0.1M sodium hydroxide solution. The adsorption capacity of the chitosan scaffold was 788-3316 mg/g.

# CHAPTER 3
# MATERIALS AND METHODS

## 3.1     MATERIALS

Chitin, sodium hydroxide pellets, sodium dodecyl sulphate and Borax were obtained from HiMedia, Mumbai. Activated carbon granular LR, activated carbon powder LR and acetic acid glacial extra pure were obtained from S.D. Fine Chemicals Limited, Mumbai. Chitosan was procured from Sigma Aldrich, Bengaluru. Butyraldehyde was obtained from Loba Chemie Pvt. Ltd., Mumbai. Methanol was obtained from Rankem, Gurgaon. Reactive red dye was obtained from the Department of Textile Technology, Kumaraguru College of Technology, Coimbatore. UV- spectrophotometer (UV-180) from Shimadzu Corporation was used to measure maximum absorbance of dye. Visible spectrophotometer (Systronics, Model 106) from was used to measure the absorbance of sample solution. To measure the pH of the solutions, pH meter (LI 120) from ELICO limited, Hyderabad, was used. Peristaltic pump (Neolab Ltd.) was used to adjust the flow rate in continuous studies.

## 3.2     PREPARATION OF BUTYL-CHITOSAN

Butyl-chitosan was prepared by the methods as given in (Martin et al., 2009) with slight modifications. About 0.5 g of chitosan was added to 15 ml of 2.5% acetic acid and the contents were stirred until the chitosan is completely dissolved. To this solution, 15 ml of methanol was added and stirred for 15 min during which 20 ml of butyraldehyde and 1.25 g of borax were added simultaneously. The mixture is continuously stirred

for 2 h and then cooled to room temperature. This mixture was then filtered using Whatman filter paper No.1 and washed with 150 ml of methanol in increments. Finally, the filtered matrix was dried at room temperature overnight.

## 3.3 CHARACTERISATION OF BUTYL-CHITOSAN

### 3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

It is an essential characterisation technique to describe the structure of matter at molecular scale. Infrared (IR) Spectroscopy is used to determine the chemical composition and the bonding arrangement of constituents of polymeric materials. IR spectrum is obtained from the FTIR spectrometers by Fourier transformation of the signal from interferometer provided with a moving mirror which produces an optical transform of the IR signal. The relation of intensity and frequency is given by numerical Fourier analysis. This relation is the IR spectrum.

## 3.4 BATCH ADSORPTION STUDIES

### 3.4.1 Effect of pH

The effect of pH is one of the prime parameter for the study of adsorption isotherm. The influence of pH on dye removal was studied. Hence the dye solution was adjusted to different pH for the study. The variable pH taken for the study was 7, 8, 9, 10 and 11. The experiment was carried out with fixed conditions of the dye concentration of 30 ppm and butyl-chitosan dosage of 0.05 g/ml for 15 min at room temperature without any agitation.

### 3.4.2 Effect of contact time

The influence of time in dye removal was the next parameter studied which gave data for adsorption kinetics studies. The dye solution was

treated with the butyl-chitosan for different periods of time. The time taken for the study was varied from 10, 20, 30, 40, 50 and 60min. The experiment was carried out with fixed conditions of the dye concentration (30 ppm) and butyl-chitosan dosage (0.1 g/ml) at pH 7 without any agitation and room temperature.

### 3.4.3    Effect of initial dye concentration

The influence of the initial dye concentration was also studied and it is an important factor to plot the adsorption isotherms. Butyl- chitosan was treated with different concentrations of the dye solution. The variable concentrations of dye taken were 30 ppm, 50 ppm, 70 ppm and 100 ppm. The experiment was carried out with fixed conditions of the butyl-chitosan dosage  (0.1 g/ml) at pH 7 without any agitation and  room temperature for 20 min.

### 3.4.4    Effect of temperature

The influence of the temperature was studied which is important for carrying out thermodynamics studies. The dye solution was treated with the butyl-chitosan at different temperatures. The variable temperatures that were taken for the study were 15°C, 20°C, 30°C, 35°C and 40°C. The experiment was carried out with fixed conditions of the butyl-chitosan dosage (0.1 g/ml), dye concentration (30 ppm) and pH 7 without any agitation for 20 min.

### 3.4.5    Effect of adsorbent dosage

The influence of adsorbent dosage was studied. The dye solution was treated with different dosages of dye. The variable dosage of dye that was taken for study was 0.1 g/ml, 0.05 g/ml, 0.0325 g/ml and 0.025 g/ml. The experiment was carried out with fixed conditions of the dye

concentration (30 ppm) and pH 7 without any agitation for 20 min at 30°C.

## 3.5    CONTINUOUS STUDY

Continuous adsorption studies were carried out using a hydrophobic interaction chromatography column packed with butyl-chitosan matrix. 1.3g of butyl-chitosan was packed in a syringe column of length 6cm and diameter 1cm. The reactive red dye solution at concentration of 30ppm was used as the mobile phase. The flow rate of the input and output was adjusted to 4ml/min using peristaltic pumps fitted at the inlet and outlet of the column. Initially, the eluent was collected for every 1 minute time interval for 30 min and then allowed  to flow through the column until the capacity of the column to adsorb the dye was decreased. The dye adsorbed on the butyl-chitosan matrix was removed by using 0.3% sodium dodecyl sulphate (surfactant) as the mobile phase.



**Figure 3.1 Experimental set-up of reactor for continuous dye removal**

## 3.6    EVALUATION OF EXPERIMENTAL DATA

### 3.6.1    Adsorption capacity ($Q_e$)

Adsorption capacity is the extent of adsorption of the solute molecules on the surface of an adsorbent. Mathematically, it is given as,

$$Q_e = \frac{(C_i - C_o)*V}{m}$$

Where, '$C_i$' is the initial dye concentration (ppm), '$C_o$' is the final dye concentration after adsorption (ppm), 'V' is the volume of dye solution used (l) and 'm' is the mass of the adsorbent used (g).

### 3.6.2    Adsorption isotherms

The adsorption isotherms are studied to determine the adsorption equilibrium data. Two adsorption isotherms are used for this purpose: Langmuir isotherm model and Freundlich isotherm model.

### 3.6.2.1    Langmuir isotherm model

Langmuir isotherm model is an empirical isotherm to determine the homogeneity of the adsorbent. It is one of the well established isotherms to determine the surface phenomena. The linear equation of Langmuir isotherm is,

$$\frac{1}{Q} = \frac{1}{Q_{max}*b*C_e} + \frac{1}{Q_{max}}$$

Where, 'Q' is the amount of dye adsorbed per unit mass of adsorbent (mg/g), '$Q_{max}$' is the Langmuir monolayer adsorption capacity (mg/g), '$C_e$' is the dye concentration at equilibrium (%w/v) and 'b' is the Langmuir constant related to intensity of adsorption.

### 3.6.2.2     Freundlich isotherm model

Freundlich isotherm model is an empirical isotherm to determine the heterogeneity of the adsorbent. The linear form of the equation is,

$$\ln Q = \ln K + (1/n) \ln C_e$$

Where, '$C_e$' is the dye concentration at equilibrium, '$Q$' is the amount of dye adsorbed per unit mass of adsorbent (mg/g), '$K$' is the adsorption capacity (mg/g), '$n$' is the adsorption intensity.

### 3.6.3     Adsorption kinetics

Adsorption kinetics studies are carried out to determine the rate controlling mechanisms of adsorption. Pseudo first order kinetics and pseudo second order kinetics models were used to determine the sorption of dye onto butyl-chitosan.

### 3.6.3.1     Pseudo first order kinetics

The pseudo first order kinetics equation for adsorption process is given by,

$$\log (Q_e - Q_t) = \log Q_e - (\frac{K_1}{2.303} * t)$$

Where, '$Q_e$' is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g), '$Q_t$' is the amount of dye adsorbed per unit mass of adsorbent at particular time (mg/g), '$t$' is the time (min) and '$K_1$' is the constant parameter.

### 3.6.3.2     Pseudo second order kinetics

The pseudo second order kinetics equation for adsorption process is given by,

$$\frac{t}{Q_t} = \frac{1}{K_2 * Q_e^2} + \frac{t}{Q_e}$$

Where, 'Q$_e$' is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg/g), 'Q$_t$' is the amount of dye adsorbed per unit mass of adsorbent at particular time (mg/g), 't' is the time (min) and 'K$_2$' is the rate constant of second order.

### 3.6.4    Adsorption thermodynamics

In order to determine the thermodynamics nature of the adsorption process, the experimental data were verified with Vant-Hoff equation. The linear form of the equation is,

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Where, $K_c = \frac{C_{Ae}}{C_e}$ , $C_{Ae}$ is the adsorbed dye concentration at equilibrium (%w/v), 'C$_e$' is the equilibrium concentration of dye in the solution (%w/v). $\Delta H^\circ$ and $\Delta S^\circ$ are the constants.

# CHAPTER 4
# RESULTS AND DISCUSSION

## 4.1     MAXIMUM WAVELENGTH FOR REACTIVE RED SOLUTION

The reactive red dye solution used for determining the maximum absorption wavelength was of concentration 20ppm and prepared in distilled water. The maximum wavelength of reactive red dye solution was determined using UV- spectrophotometer by measuring its absorbance for a range of wavelength from 300-800 nm. The results obtained showed the maximum absorbance for reactive red dye solution to be 500nm.
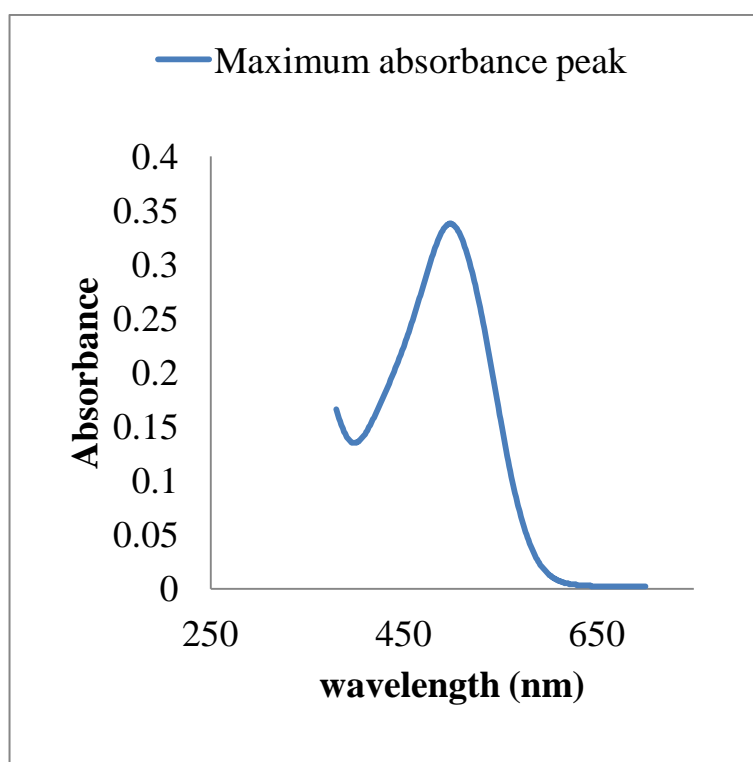


**Figure 4.1 UV-Visible absorption spectrum of reactive red**

## 4.2    STANDARD    CURVE    FOR    REACTIVE    RED    SOLUTION

In order to determine the molar absorption coefficient, a standard curve with different concentrations of dye solution is plotted. According to Beer Lambert's law, the quantity of light absorbed by a substance dissolved in a fully transmitting solvent is directly proportion to the concentration of substance and the path length of the light through the solution. Mathematically it is given as,

$$A = \varepsilon \, l \, C$$

Where, 'A' is the absorbance at 500 nm, 'l' is the path length of light through the solution, 'C' is the dye concentration (%w/v) and '$\varepsilon$' is the molar absorption coefficient.

The calculation of molar absorption coefficient is done to calculate the concentration of dye solution from the corresponding absorbance values.
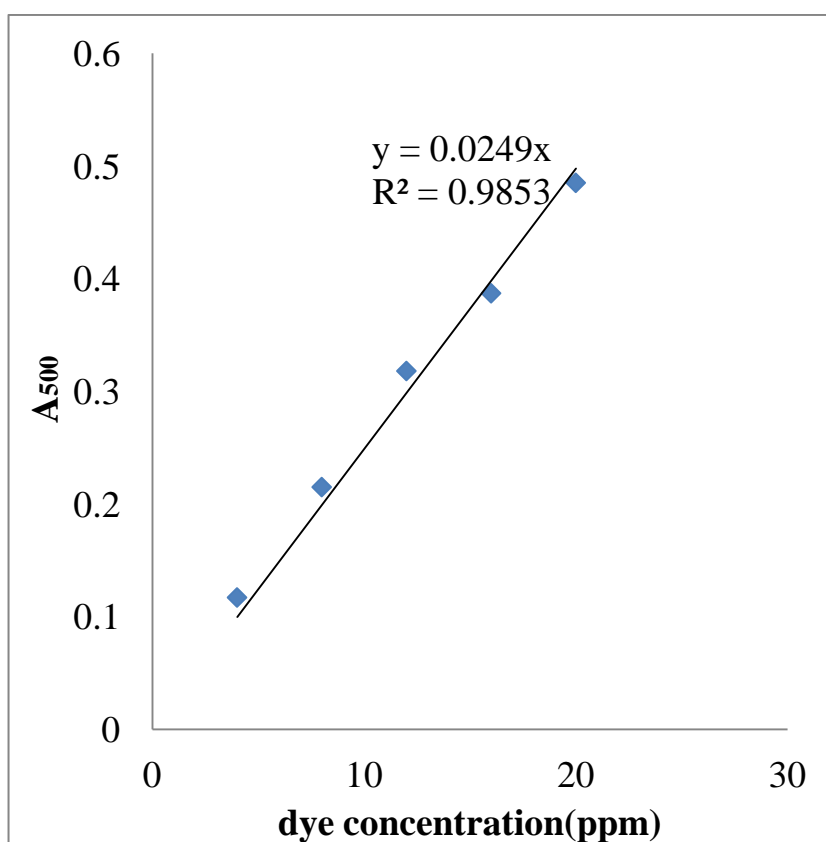


**Figure 4.2 Standard curve for reactive red dye solution**

## 4.3 CHARACTERISATION OF BUTYL-CHITOSAN

### 4.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Butyraldehyde was coupled to amino group of chitosan to form butyl-chitosan which was characterized using FTIR spectra. The FTIR spectra of chitosan before and after the analysis are as shown in figures 4.2 and 4.3. Coates (2000) provided a complete set of data on the frequencies of different functional groups. The FTIR spectra of commercial chitosan showed a peak at 3417 cm$^{-1}$ corresponding to the N-H stretch. A shift in this peak was found in the FTIR spectra obtained for the prepared butyl-chitosan. This gives the evidence of incorporation of butyl group with -NH$_2$ group at C2 position in chitosan. Nuclear Magnetic Resonance (NMR) and Scanning Electron Microscopy (SEM) analysis can also be carried to confirm the incorporation of butyl group with chitosan.
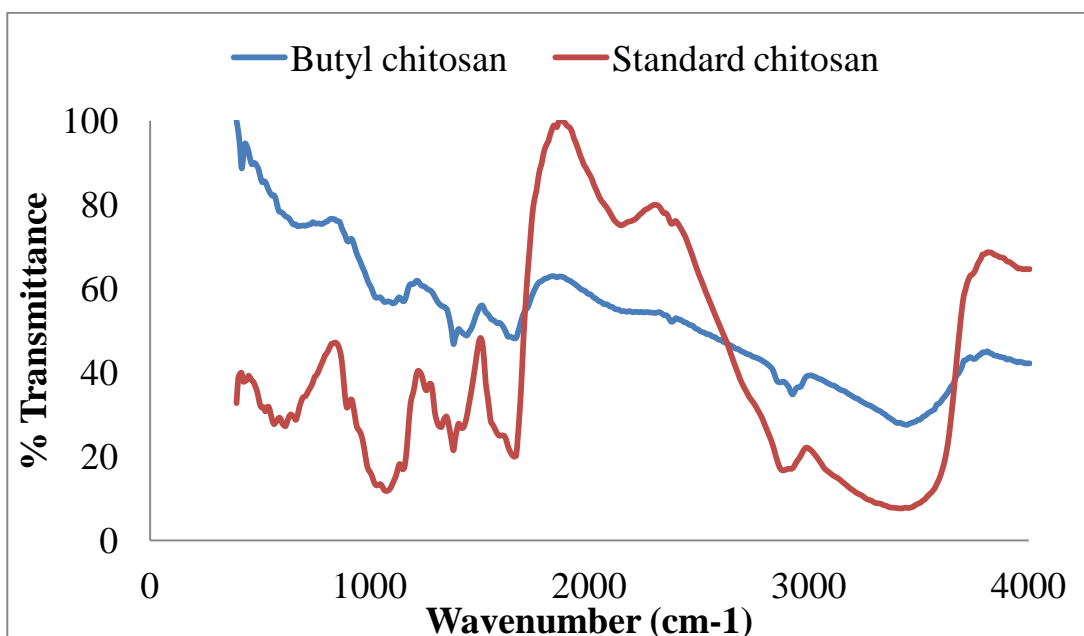


**Figure 4.3 FTIR spectra of standard chitosan and butyl-chitosan**

## 4.4　　　BATCH ADSORPTION STUDIES

### 4.4.1　　Effect of pH

The pH of the dye is considered to be one of the most important parameters for the study of adsorption. The original pH of the dye was found to be 7.46. From the fig. 4.4, it is found that the maximum dye removal was at pH 7 with a dye removal percentage of 45.9. And also it is evident that the percentage dye removal decreased with an increase in the pH. Jabbar *et al*., (2014) carried out the removal of congo red dye from aqueous solutions using chitosan. The highest percentage dye removal was 80.85% at pH 2. Huang *et al*., (2011) studied the removal of methylene blue using cross-linked succinyl chitosan as an adsorbent. The highest adsorption percentage was found at pH 6.
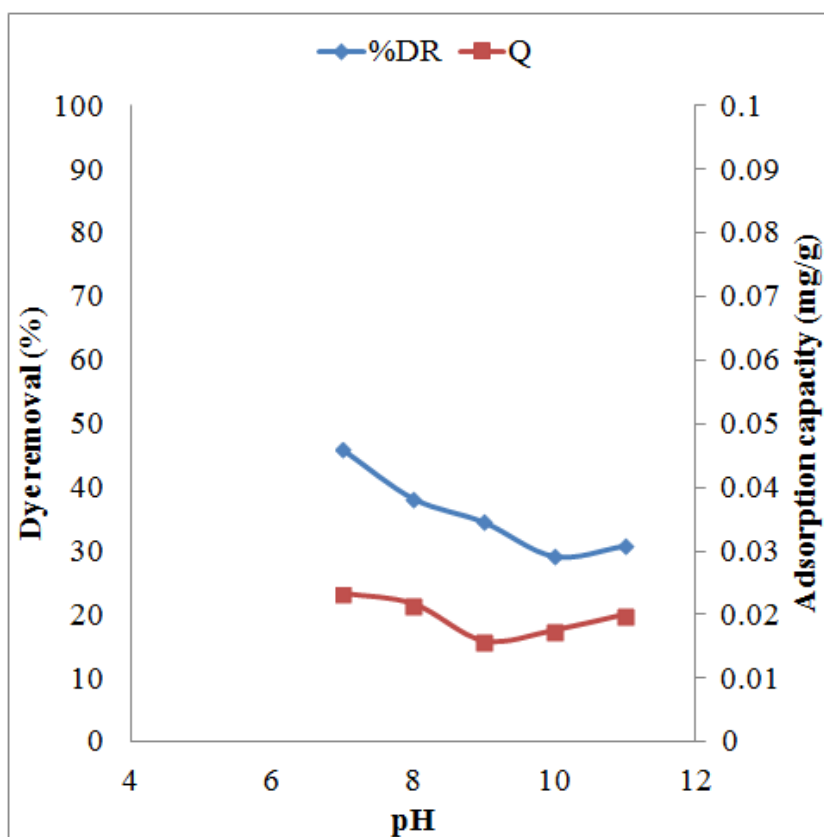


**Figure 4.4 Effect of pH on adsorption of dye using butyl-chitosan**

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### 4.4.2    Effect of contact time

The effect of contact time for the adsorption study was determined by varying the time from 10 to 60 min. It was found that the maximum dye adsorption was at the $20^{th}$ minute with a percentage of 73.77. This is due to saturation of active adsorption sites which do not allow further adsorption to occur. It is determined that the adsorption was maximum at the optimum time and decreased further as the time increased. Jabbar *et al*., (2014) investigated the removal of congo red dye using chitosan and found maximum dye removal of 80.6% at 140 min. Huang *et al*., (2011) while investigating the adsorption of methylene blue onto cross-linked succinyl chitosan, found the adsorption rate to be relatively fast and high in first 5 min.
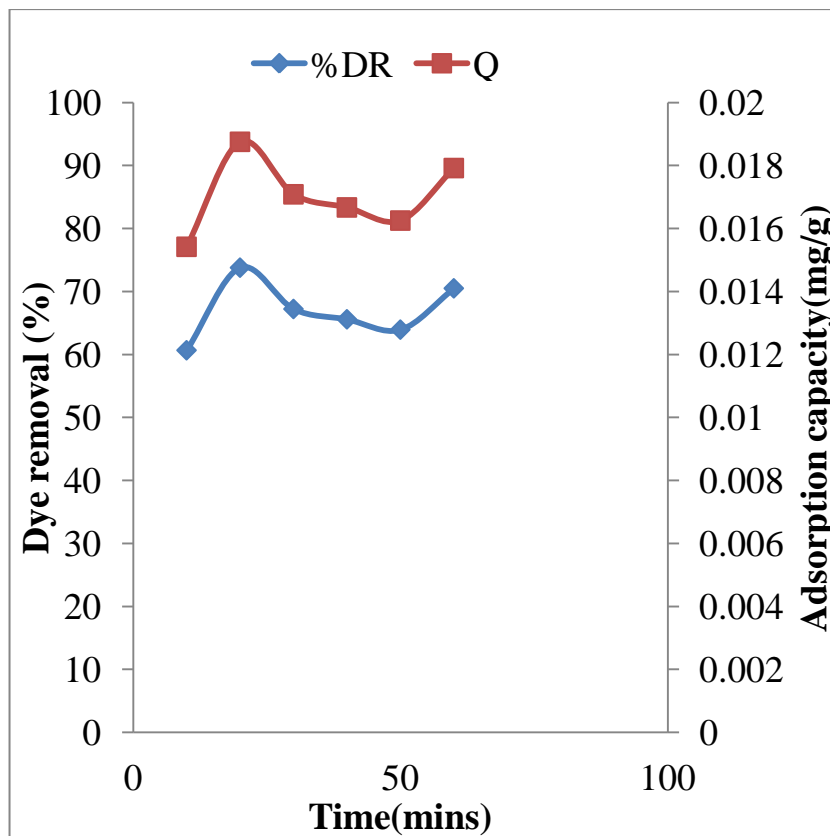


**Figure 4.5 Effect of contact time on adsorption of dye using butyl-chitosan**

### 4.4.3 Effect of initial dye concentration

From the fig. 4.6, we infer that as the dye concentration increases the adsorption decreases. The maximum dye removal percentage of 77.42 was obtained when the dye concentration was 30ppm. This was caused by an increase in the mass gradient pressure between the dye solution and adsorbent. This gradient provided the force that resulted in the transfer of dye molecules from the bulk solution to butyl-chitosan surface. Hence, 30ppm was the optimum dye concentration for the removal of dye. Jabbar *et al*., (2014) reported maximum dye removal of 82.02% at 10 mg/l initial dye concentration while investigating the removal of congo red dye using chitosan. Huang *et al*., (2011) investigated the removal of methylene blue using cross linked succinyl chitosan and found that 1g of cross linked succinyl chitosan adsorbs 281.58mg of methylene blue.
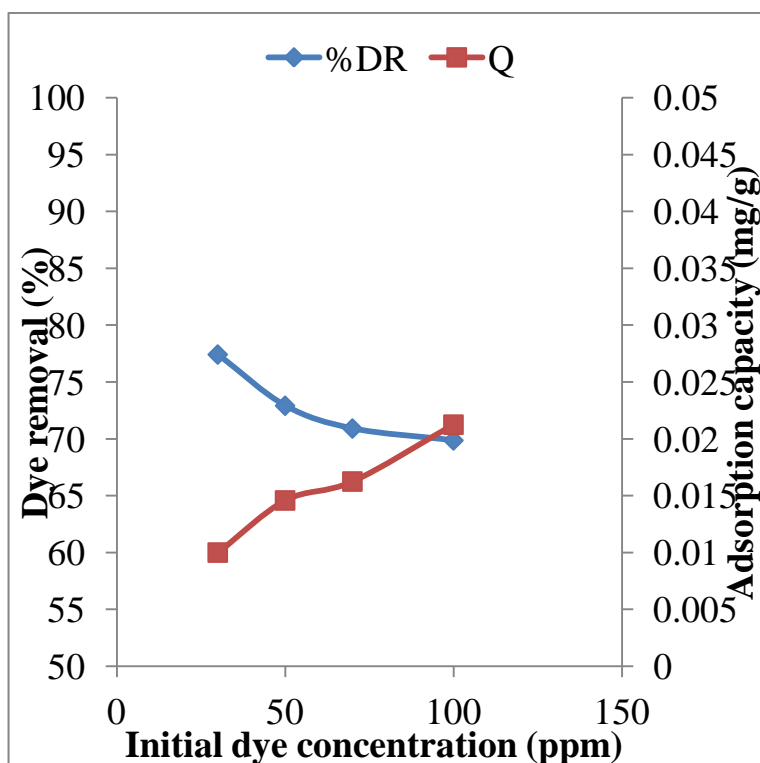


**Figure 4.6 Effect of initial dye concentration on adsorption of dye using butyl-chitosan**

### 4.4.4　　　Effect of temperature

Temperature has an important effect on adsorption process. As the temperature increased, the percentage dye removal also increased. It is evident from the fig. 4.7 that the percentage dye removal was maximum between 30°C and 40°C with the percentage of 74.9. Hence, 30°C was used as an optimum temperature for further studies. From the studies conducted by Huang *et al*., (2011) on the removal of methylene blue using succinyl chitosan, it was inferred that the maximum adsorption of methylene blue occurred at room temperature (298K).
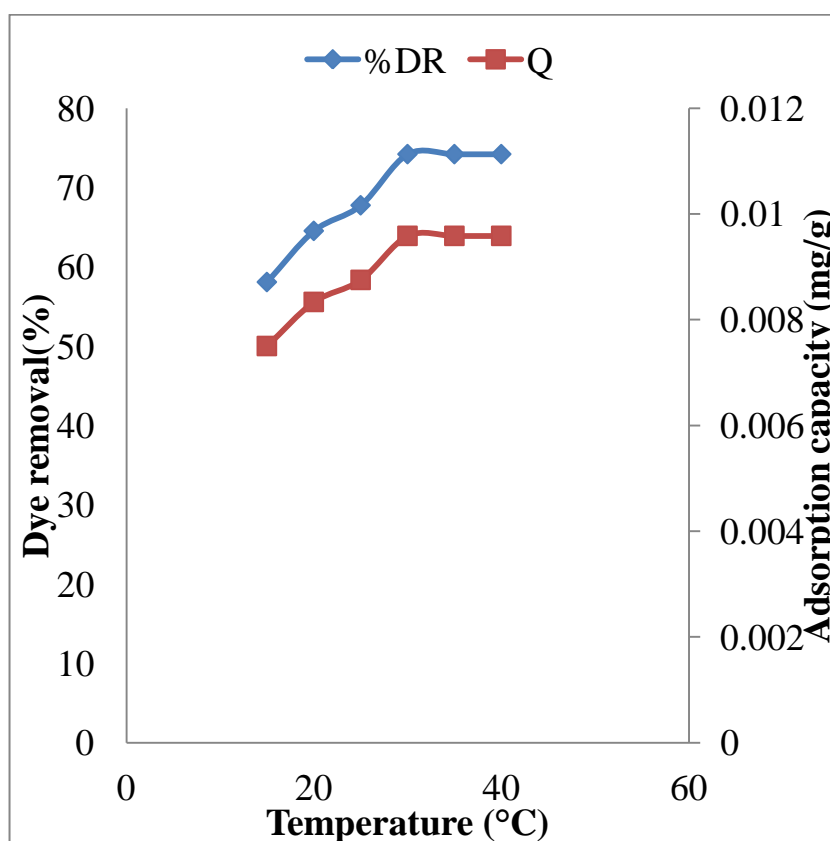


**Figure 4.7 Effect of temperature on adsorption of dye using butyl-chitosan**

### 4.4.5 Effect of adsorbent dosage

The amount of butyl-chitosan added to the dye plays a significant role in dye removal. The dye removal increases with an increase in amount of adsorbent added to it. The adsorbent dosage was optimized to be 0.1 g/ml with a percentage removal of 64.52. The fig. 4.8 shows that the dye removal percentage increases as the amount of adsorbent increases. This result is expected because with increase in adsorbent dosage, the availability of adsorption sites and adsorbent surface area increases, thus increasing the adsorption of dye. Jabbar *et al*., (2014) while studying the removal of congo red dye using chitosan reported 86% removal at adsorbent dosage of 0.25g.
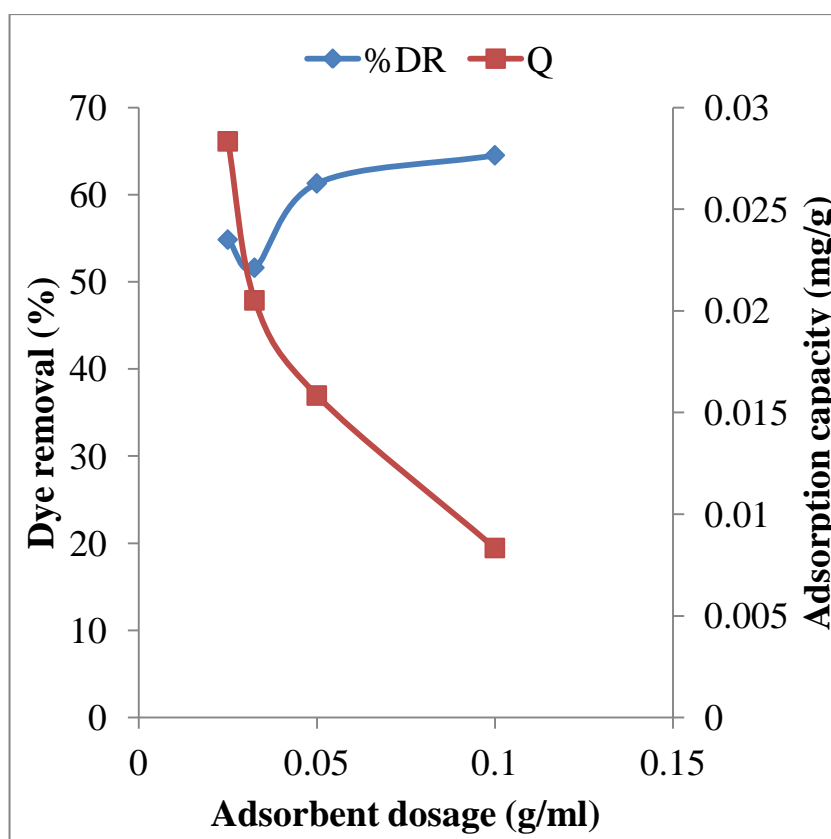


**Figure 4.8 Effect of adsorbent dosage on adsorption of dye using butyl-chitosan**

## 4.5      ADSORPTION ISOTHERM STUDIES

In order to study the surface phenomena of the adsorption process, Langmuir and Freundlich isotherm models were carried out.

### 4.5.1      Langmuir isotherm model

Langmuir adsorption model was analyzed to study the homogeneity of the adsorbent.  It is evident from fig. 4.9 that  the adsorption data fitted the adsorption isotherm model. From the linear equation of the model it was determined that the Langmuir monolayer adsorption capacity, $Q_{max}$ was 0.0375 mg/g and the Langmuir constant; b was 0.813, which is the measure of intensity of adsorption. Huang *et al*., (2011) reported $Q_{max}$ of 289.03 mg/g and b of 1.922 l/mg for Langmuir adsorption studies for methylene blue dye removal using succinyl-chitosan.
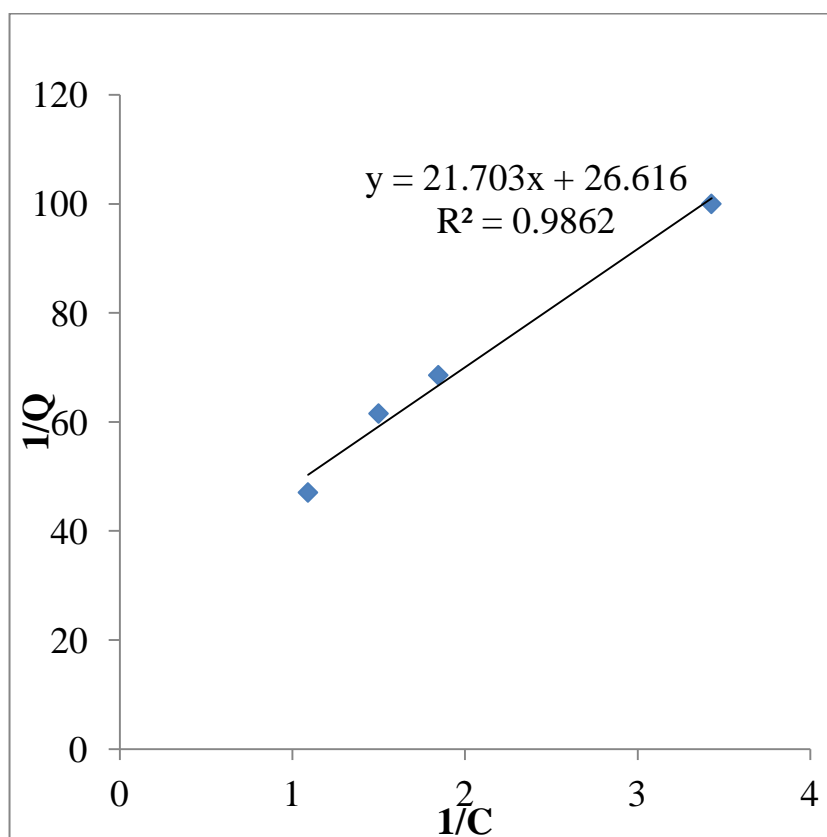


**Figure 4.9 Langmuir isotherm model for adsorption of dye onto butyl-chitosan**

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## 4.5.2      Freundlich isotherm model

Freundlich adsorption isotherm model is an empirical isotherm which is used to determine the heterogeneity of the adsorbent. From the data and the fig. 4.10 as given below, it is inferred that the adsorption data fitted the isotherm model. The linear equation determined the Freundlich adsorption capacity, K to be 0.022 mg/g and the intensity of adsorption, n was 1.55 which is also the measure of intensity of adsorption. Huang *et al*., (2011) found that K and n were 149.44 l/g and 3.38 at 298K, respectively for the removal of methylene blue using succinyl-chitosan.
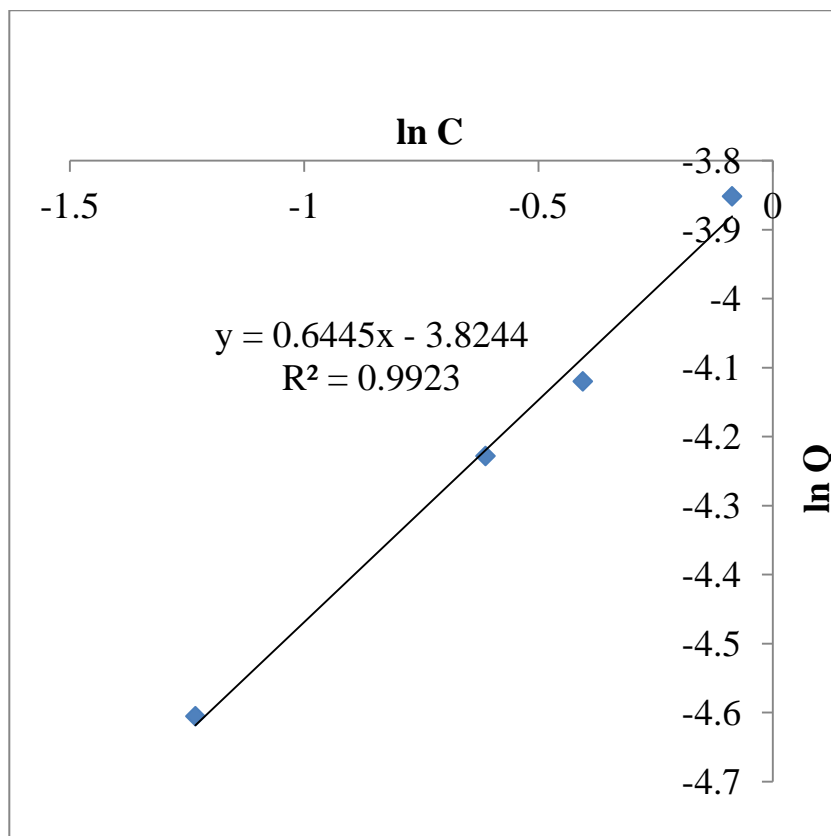


**Figure 4.10 Freundlich isotherm model for adsorption of dye onto butyl-chitosan**

## 4.6      ADSORPTION KINETICS STUDIES

Adsorption kinetic studies are carried out to determine the rate controlling mechanisms of adsorption. Pseudo first order and Pseudo-second order kinetics models were checked with the experimental data for the best fit. It was found that the adsorption data did not fit the pseudo first order kinetics model. Thus, pseudo-second order kinetics was tested. The pseudo-second order kinetics was the perfect fit for the experimental data. From the model, the adsorption capacity at equilibrium, $Q_e$ was found to be 0.017 mg/g and the rate constant of second order reaction was 0.0095. Huang *et al*., (2011) in their adsorption kinetics study found rate constants, $K_1$ to be 0.0135/min and $K_2$ to be $6.71 \times 10^{-3}$ g/(mg min).
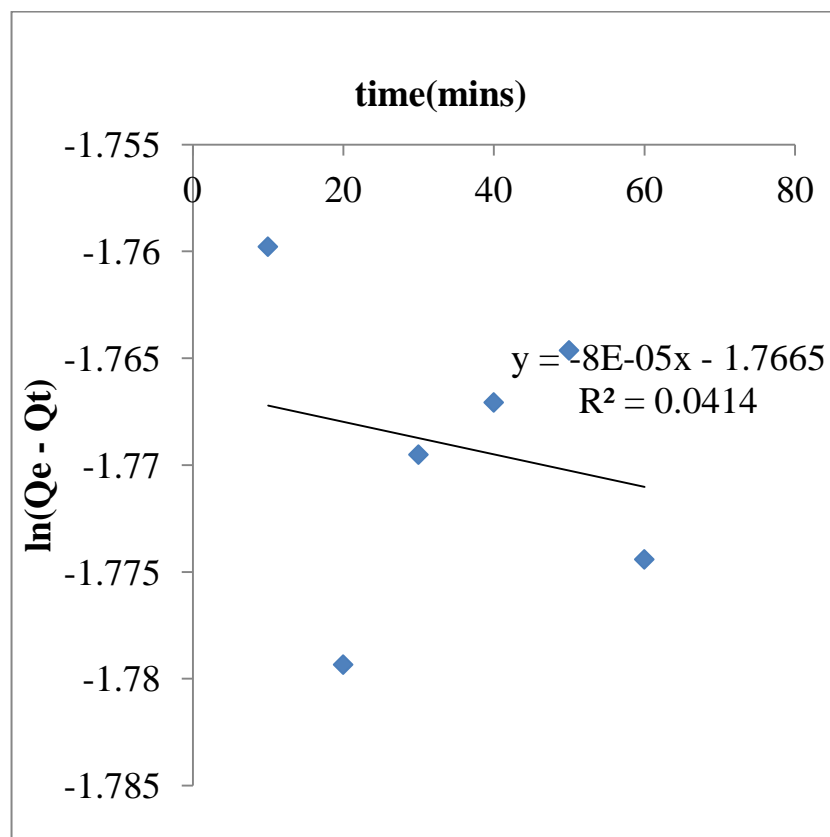


**Figure 4.11 Pseudo first order kinetics model for adsorption of dye onto butyl-chitosan**
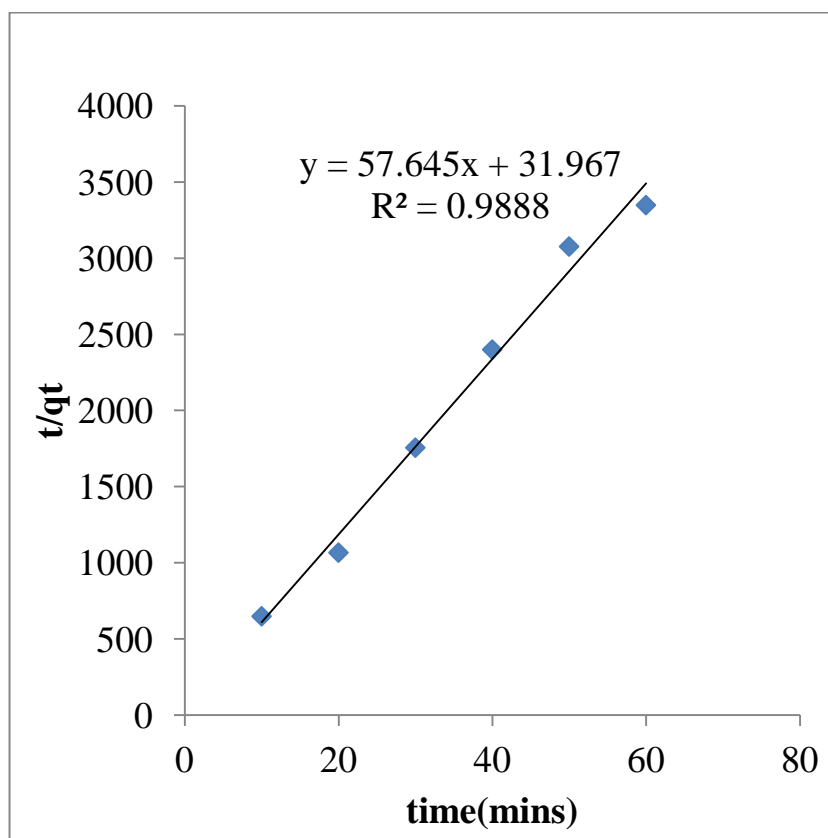
**Figure 4.12 Pseudo second order kinetics model for adsorption of dye onto butyl-chitosan**

## 4.7     ADSORPTION THERMODYNAMICS STUDIES

To determine the thermodynamic data of the adsorption process, Vant-Hoff equation was used. From the experimental data and the fig. 4.13, the constants $\Delta H°$ and $\Delta S°$ were calculated. From these values the Gibbs free energy $\Delta G°$ was calculated and found to be negative at 30°C. Thus it was evident that the adsorption process is favourable at 30°C. Huang *et al*., (2011) reported the adsorption of methylene blue onto succinyl chitosan to be a spontaneous process and less favourable at higher temperatures.
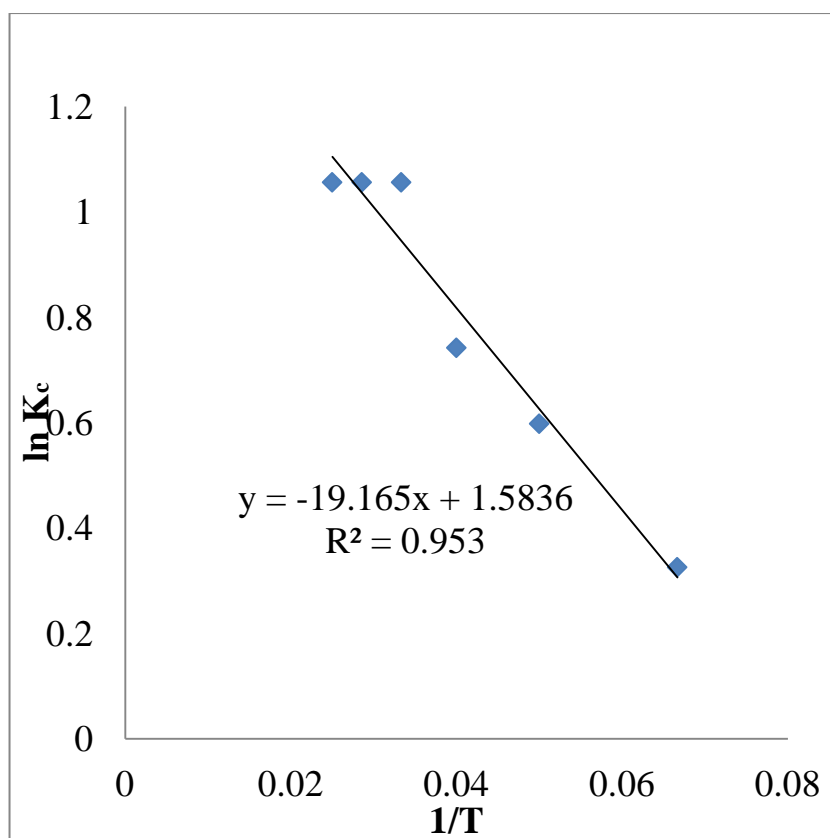
**Figure 4.13 Adsorption thermodynamics for adsorption of dye onto butyl-chitosan**

**Table 4.1 The constants evaluated using the adsorption isotherm, kinetics and thermodynamics data**

| S.No. | Adsorption studies | Model | Parameters | $R^2$ |
|-------|--------------------|-------|------------|-------|
| 1. | Isotherm | Langmuir | b=0.813<br>$Q_{max}$=0.0375 | 0.9862 |
|  |  | Freundlich | K=0.0218<br>n=1.5515 | 0.9923 |
| 2. | Kinetics | Pseudo second order kinetics | $K_2$=0.0095<br>$Q_e$=0.0173 | 0.9888 |
| 3. | Thermodynamics | Vant-Hoff | $\Delta H°$=159.33<br>$\Delta S°$=13.166 | 0.953 |

**Table 4.2 Comparison of % Dye removal of various materials**

| S.No. | Adsorbent | Dye removal (%) | Adsorption capacity (Q) |
|-------|-----------|-----------------|--------------------------|
| 1. | Chitin | 20.4 | 0.008 |
| 2. | Chitosan | 42.8 | 0.0175 |
| 3. | Butyl-chitosan | 77.4 | 0.01 |
| 4. | Activated carbon Granules | 62.19 | 0.0425 |
| 5. | Activated carbon powder | 85.4 | 2.91 |
| 6. | Octyl-sepharose | 95.34 | 0.044 |
| 7. | Butyl-sepharose | 96.06 | 0.044 |
| 8. | Phenyl-sepharose | 95.86 | 0.097 |

From the table 4.2, it was figured out that chitin showed the lowest ability for the removal of reactive red dye solution and butyl-sepharose showed the highest. Butyl-chitosan when compared with commercial chitosan showed better removal of the dye from effluent. This is due to the presence of hydrophobic groups (butyl) with9 chitosan, leading to increased adsorption of the basic dye. But when comparing butyl-chitosan to activated carbon, its efficiency is less. Also, activated carbon powder showed better results when compared to activated carbon granules. This is because of the larger surface area of powdered activated carbon. Also, the sepharose family showed the highest percentage dye removal. Sepharose is highly expensive and hence is not a preferred adsorbent though its dye removal efficiency is high. Activated carbon is an excellent source for dye removal and with availability of low-cost sources of activated carbon; it has become a highly preferred material for dye removal. The disadvantage of using

activated carbon lies in the scale-up process. Batch adsorption studies cannot be carried out in industrial level. Also, regeneration of the activated carbon poses as a serious problem. If activated carbon is packed in a column and used as a column material, choking would occur due to its fine particle size. Thus for industrial level, another better alternative would be a hydrophobic column packed with acylated chitosan like butyl-chitosan.

## 4.8     CONTINUOUS STUDY

The experiment was carried out with 1.3 g of butyl-chitosan matrix packed in syringe column (6 ml). About 200 ml of dye was allowed to pass through the    at flow rate of 4ml/min for a period of 2 h. The absorbance was taken at 500nm for 3ml eluent was collected every one minute for the first 30 min. The maximum dye removal for these samples was found to be 96.77%  between the fractions  7 min and 30 min time interval. It was found that the flow rate of eluent decreased drastically. The dye removal percentage at the end of 2 h was 90.32. In other words, about 90% of the dyes were bound to the column matrix. This showed that continuous column processes can be utilised for industrial applications for removal of dye. The results are quite encouraging and for the first time in the literature such studies are carried out by us for continuous  removal of dyes using column studies. Further, scale-up studies need to be carried out to implement these results at industrial-level.

# CHAPTER 5

# CONCLUSION

The aim of the project was to investigate the efficiency of acylated chitosan for the removal of dye. In this work, butyl-chitosan was prepared and utilized for the removal of reactive red dye. The adsorption studies were carried out in both batch and continuous mode. The batch adsorption studies were carried out at varying conditions of pH, temperature, contact time, initial dye concentration and adsorbent dosage to find the optimum conditions for the dye removal. The results of the batch studies showed maximum dye removal of 67.5% at pH 7, 0.1 g of butyl chitosan/ml, 30ppm dye concentration and 30°C for 20 min without agitation. Since batch adsorption studies are difficult to be scale-up, continuous study was also investigated. The butyl-chitosan matrix column showed better dye removal efficiency when compared to batch studies. The maximum dye removal percentage was 96.77% between the fractions 7 min and 30 min time interval. At the end of 2 h, the dye removal efficiency was 90.32%. Thus this method of dye removal can be used for industrial applications.

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